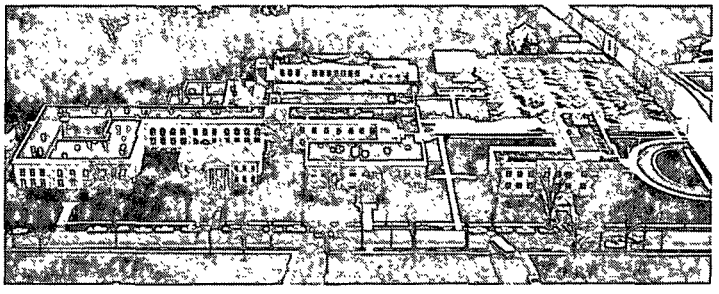

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Formation and Identification of cis/trans Ferulic Acid in Photoyellowed White Spruce Mechanical Pulp

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Abstract

Direct studies of photoyellowed unbleached white spruce refiner mechanical pulp have been carried out using laser Raman spectroscopy, GC mass spectrometry and Fourier transform infrared spectroscopy (FTIR) techniques. A new chromophore, namely, ferulic acid has been detected. The experimental results indicate the presence of both cis and trans isomers of ferulic acid. The former, because of its yellow color, is considered to be a contributor in the yellowing process.

Introduction

The topic of photoinduced brightness reversion (yellowing) of high-yield pulps is of great interest to the pulp and paper industry. Color reversion refers to the yellowish appearance which is developed in these pulps upon exposure to light in the presence of molecular oxygen. Unknown photochemical reactions involving the pulp components and O_2 cause yellowing and are responsible for the pulp's lower brightness. Pulp with potential for low brightness is undesirable for a wide range of applications. Furthermore, in several applications, substitution of high-yield pulps for chemical pulps is limited for the same reason.

Although numerous studies carried out in the past have enhanced our understanding of the color reversion phenomenon, the causes and mechanisms of yellowing are not yet well understood. It has been known for a long time [1-6] that lignin in the pulp is the primary factor in the photoinduced color reversion.

On the basis of earlier work, quinone type structures were thought to be formed [4,7-9]. More recently O-quinonoid structures have been found to exist in the yellowed pulp [10]. A review of the literature on the topic reveals that the understanding of the process remains incomplete. For example, the identities of many chromophores are not known, nor are the natures of various pathways that the system moves through after initial ultraviolet excitation. Because of the complexity of lignocellulosics, direct studies of lignin photobehavior are almost nonexistent. Nevertheless, detailed studies of lignin model compounds abound [6,11-13]. Such investigations have enhanced our knowledge with regard to what may take place in pulp. However, in view of the fact that the photobehavior of aromatic compounds is sensitive to changes in their physical and chemical surroundings [14], it is not always clear under what experimental conditions the models will best simulate lignin photobehavior. This view is underscored by a recent study of lignin model compounds by Castellan et al. [15], who have shown that a change in the environment/medium could lead to modified photobehavior.

In this report, we describe results of our in situ studies of white spruce refiner mechanical pulp (RMP) handsheets. The objective here was to identify chromophores which contribute to photoyellowing of pulp sheets. A number of analytical techniques including Raman spectroscopy, GC mass spectrometry, and FTIR were used. In the Raman spectral studies, a unique sampling procedure has paved the way for obtaining novel results.

Experimental

Both yellowed and unyellowed white spruce handsheets were used in this work. Handsheets were made from unbleached white spruce refiner mechanical pulp

in accordance with TAPPI standard 205 om-81. This pulp had earlier been treated by ethylenediaminetetraacetic acid (EDTA), extracted in ethanol/benzene and washed in distilled water. The treatments with EDTA and ethanol/benzene were, respectively, to remove metal ions and extractives from the pulp. Photoirradiation of handsheets was carried out by using an ORIEL 1000 W solar simulator fitted with an "air mass one" filter. The sheets were exposed at a chosen irradiance level for 20 hr under controlled conditions (RH 50%, temperature 21°C). Additional details are provided in reference 16. Although the sheets were studied directly using Raman and FTIR spectroscopy, only their extracts were used in the GC/mass spectrometry measurements.

Raman spectra were obtained on an Instruments SA Ramanor HG2S system using the 514.5 nm line of an Ar ion laser. Samples were mounted in homemade cells through which oxygen could be flushed. Oxygen flushing was used in order to reduce the background contribution to the total signal. This sampling technique was developed by us, and has proven effective for quenching background luminescence in lignocellulosics [17].

The GC/mass spectrometric analyses were carried out using a Hewlett-Packard GC MS 5985B system. Samples were prepared from handsheets either by a laser desorption technique (argon ion laser used) or by direct extraction in methanol. In laser-induced thermal desorption the sheet surface is subjected to a rapid temperature jump, during which neutral species are vaporized from the surface [18]. These desorbed molecules are in turn solvated by the surrounding solvent molecules. Methanol extracts produced in this fashion were concentrated by bubbling pure dry nitrogen gas, and were silated using standard procedures. Sample preparations were carried out in the dark in order to avoid any photochemically induced reactions.

The FTIR work was carried out on a Nicolet 7199 spectrometer. Spectra were obtained in one or more of the following sampling modes: diffuse reflectance infrared Fourier transform (DRIFT), thin film, and KBr pellet.

Brightness measurements were made in accordance with TAPPI standard T 452 om-83 at an effective wavelength of 457 nm. The data were obtained using a common backing pad for all samples studied.

Ferulic acid was obtained from Aldrich Chemical Company and was recrystallized from methanol before use. A mixture of cis/trans ferulic acid was produced by exposing the methanol solution of predominantly trans ferulic acid to the solar simulator until the two isomeric forms achieved equilibrium. Equilibrium was considered to have been reached when continued irradiation of the solution did not result in further alteration of the cis-to-trans isomer ratio. The isomeric amounts were determined by gas chromatography and gave a cis-to-trans ratio of 0.714.

Results and Discussion

The Raman spectrum of a yellowed sheet recorded under oxygen flushing conditions is shown in Fig. 1(a). As oxygen flushing was continued for an additional 24 hr, no evidence for temporal changes in the Raman features was detected. However, the background signal, as expected, showed a steady decline. Such a reduction in background signal is generally exhibited by lignocellulosic materials [17], and is indeed desirable for better signal-to-background ratios. Temporal invariance of the Raman spectral features was interpreted to mean that the spectrum did not arise as a result of laser and/or oxygen induced chemical changes in the substrate. Further evidence in support of this conclustion, based on GC/mass spec. and FTIR studies is presented below.

The spectrum of a nonyellowed sheet, obtained under identical conditions, is shown in Fig. 1(b). This sample, used as a control, possesses spectral features typical of lignocellulosics [19] and quite different from the spectrum of the yellowed specimen. The spectral region between 1050 and 1650 cm^{-1} is particularly different. This suggests that the photoyellowed surface contains species that are substantially different from their precursors.

(Figure 1 here)

In order to assign the features in the spectrum in Fig. 1(a), Raman spectra of a number of compounds that could be responsible for yellowing were compared. These included O and p-benzoquinones and disubstituted biphenyls. These efforts were unsuccessful, so a Raman study of lignin model compounds was undertaken. This was suggested by the strong aromatic ring stretching band at ~ 1600 cm^{-1}. Raman data on a number of lignin models were acquired. A simple comparision of the spectrum of ferulic acid [Fig. 2(b)] with that of the yellowed sample [Fig. 2(a)] resulted in the suggestion that this compound is most likely present in the sheet sample. Figure 2 shows these spectra, along with that of the control, plotted in the 1050-1750 cm^{-1} interval. Table 1 lists various peak positions for this set of spectra.

(Figure 2 and Table 1 here)

In order to address the question of sample alteration under Raman sampling conditions, infrared spectra of the yellowed sample were recorded both before and after the Raman studies [Fig. 3(a) and (b)]. Since it was not possible to precisely locate the region from which Raman spectra were obtained, four IR spectra in the general area of Raman measurements were acquired. These four spectra were identical, and no significant differences between this set and the

one recorded before laser exposure could be discerned. This supports our earlier thinking that the 514.5 nm laser line in the presence of molecular oxygen did not produce changes in the sample.

(Figure 3 here)

Having shown the presence of ferulic acid in the yellowed sample, its role in color reversion phenomena needed to be established. Ferulic acid is known to exhibit photoinduced cis/trans isomerization [20] and the cis form is yellow in color [21]. In view of this, we hypothesized that a portion of the yellowing that occurs on exposure to light may arise from the cis conformer.

In order to test this hypothesis, efforts were focused on detecting cis and trans ferulic acids in the yellowed sheet. GC mass spectrometry was considered ideally suited because of its high specificity and great sensitivity. Concentrated sheet extracts, which were obtained by laser desorption of material from both yellowed and nonyellowed sheets in methanol, were silated using standard procedures [22]. Such samples were then analysed by GC mass spectrometry. In addition, similar studies on extracts obtained without laser desorption were carried out.

Figure 4 shows a number of chromatograms including that of a laser desorbed yellowed sheet extract, a laser desorbed nonyellowed sheet extract (used as a control), and a mixture of cis/trans ferulic acid. Upon comparison of Fig. 4(b), (c), and (d) one finds peaks for both cis and trans conformers in the yellowed sample chromatogram [Fig. 4(c) and Table 2]. On the other hand, peaks present in the control are found not to match those of ferulic acid as is evident from Table 2. Table 2 lists characteristic ions found in mass spectra of separated chromatogram peaks of silated samples.

(Figure 4 and Table 2 here)

In the initial phase of GC/mass spec. studies, as described above, we have used laser induced thermal desorption in order to dissolve the substance from the surface of the paper sheets. In later work, however, it was thought that perhaps a sufficient sample for GC/mass spec. analysis could be obtained by simply using a larger amount of solvent. In view of this, the yellowed and control sheets were immersed in excess methanol for a week. The resulting solutions were concentrated by bubbling pure nitrogen gas. These samples were analyzed for ferulic acid using the selective-ion monitoring technique [Fig. 5]. Confirmation of trans ferulic acid in the yellowed sheet extract was made by comparing observed relative ion abundances to those for authentic trans ferulic acid [Fig. 6]. In the case of the cis conformer, however, the ratios were not the same. Nonetheless, characteristic mass spectral peaks corresponding to this isomer were seen [Fig. 5]. There could be several reasons for this. The primary reasons, we feel, are its low concentration and the presence of an impurity that has some common mass peaks.

(Figures 5 and 6 here)

In order to compare the laser desorption and direct methanol extraction modes, TAPPI brightness measurements on handsheets were made. These measurements were made on photoyellowed handsheets both before and after a particular extraction method. In addition, brightness of an unyellowed sheet was measured. Such results are shown in Table 3.

(Table 3 here)

In Table 3, the laser desorbed sheet shows higher TAPPI brightness as compared to one directly extracted in methanol. This suggests the usefulness of

the former procedure in removing chromophores from the sheet surface. Direct methanol extraction of the yellowed sheet, on the other hand, does not seem to have removed any significant amount of color causing material.

The low amount of cis-ferulic acid in the sample extract obtained by direct methanol extraction is supported by the brightness data in Table 3, where this extraction procedure did not result in any significant change in the sheet's brightness value. The lower concentration of cis could be a direct reflection of its stronger adsorption in the pulp as compared to the acid's trans counterpart. This is likely in view of the effect of structure on chemical reactivity [23]. In this regard it must be noted that molecules containing phenolic and carboxylic groups are known to be strongly adsorbed on cellulosic substrates [24]. Moreover, the equilibrium concentration of cis ferulic acid at the sheet surface could be lower to begin with.

Thus analyses of sheet sample extracts by GC/mass spec. support our findings obtained by using the laser Raman technique. Therefore, on the basis of the above work, it may be concluded that the photoyellowed handsheets made from white spruce contain both cis and trans ferulic acid.

Finally, we carried out infrared spectroscopic analyses of our samples. The initial IR studies made it clear that the spectral changes resulting from yellowing were subtle and, at best, interpretation of infrared data would be supportive in nature rather than confirmatory [25].

Depicted in Figure 7 are spectra of (A) a yellowed sheet, (B) t-ferulic acid adsorbed on a nonyellowed sheet, (C) an unyellowed sheet, (D) a cis/trans equilibrated ferulic acid mixture, and (E) t-ferulic acid. A comparision of various features, in the region 1500-1800 cm^{-1}, is presented in Table 4.

Upon photoyellowing, the only noticeable changes are reduction in the 1662 cm^{-1} band intensity and appearance of a new feature at 1680 cm^{-1} [Fig. 7(A) and (C)]. The new feature at 1680 cm^{-1} can be accounted for in terms of a ferulic acid band at the same frequency. It appears in the IR spectra of all ferulic acid containing samples, i.e., Fig. 7(B), (D), and (E). Infrared spectra of trans as well as the cis/trans mixture of ferulic acid show many features that are also seen in the IR spectra of spruce handsheets. This is not totally unexpected in view of the structural similarity between ferulic acid and the molecular structure of lignin [26].

(Figure 7 and Table 4)

The FTIR studies lend support to the other experimental evidence for ferulic acid. Although only limited information is available through IR analysis, the fact that it supports our other findings is noteworthy.

In the end, an explanation is in order for the absence of evidence for quinone type structures in our experimental work. Recently, such structures have been shown to be relevant in photoinduced brightness reversion phenomena [10]. Although it is too early to form an opinion on this matter, it is fair to say that the procedures and techniques used here may not have been the best suited for detection of quinones. In light of these observations, it appears that more than one class of structures may be responsible for yellowing. In any event, further studies to address these questions are needed.

Conclusion

A number of physical methods have been used to study photoyellowed and nonyellowed unbleached white spruce pulps. In the yellowed pulp, a new chromophore, namely ferulic acid, has been detected. Both cis and trans isomers have

been found to occur as would be expected on the basis of the photochemistry of ferulic acid. In view of the yellow color of cis-ferulic acid, its role in color reversion processes needs to be evaluated further.

Acknowledgments

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Figure captions

Fig. 1 Raman spectra of yellowed (a) and unyellowed (b) white spruce handsheet samples obtained under molecular oxygen atmosphere.

Fig. 2 Raman spectra in the region 1050-1750 cm^{-1} shown on expanded frequency scale; (a) yellowed sheet; (b) ferulic acid; (c) unyellowed sheet. Ferulic acid molecular structure is also shown.

Fig. 3 Typical infrared spectra obtained from yellowed sample (a) before and (b) after Raman experiment.

Fig. 4 Chromatograms of silated samples; (a) t-ferulic acid; (b) cis/trans ferulic acid mixture; (c) yellowed handsheet extract; (d) control or nonyellowed handsheet extract.

Fig. 5 Ferulic acid detection by selective-ion monitoring; nonyellowed handsheet extract (a), and yellowed handsheet extract (b) obtained with out using a laser.

Fig. 6 Relative ion abundances of several ferulic acid ions in (a) yellowed handsheet extract, and (b) trans-ferulic acid.

Fig. 7 Infrared spectra of (A) yellowed sheet; (B) unyellowed sheet + (trans-ferulic acid); (C) unyellowed sheet; (D) cis/trans ferulic acid mixture; (E) trans-ferulic acid.

Table 1. A comparison of Raman band frequencies (cm^{-1}) of samples whose spectra are shown in Fig. 2.

Figure 2(a) Yellowed Sheet	Figure 2(b) Ferulic Acid	Figure 2(c) Nonyellowed Sheet
		1094 w
1120 w	1122 w	1120 m, br
		1150 w, sh
1165 sh	1163 sh	
1175 s	1175 s	
1240 m	1240 m	
1271 s	1270 s	1275 w, br
		1335 w, br
1375 w	1375 w	1380 w, br
1420 sh	1420 sh	1420 w, br
1432 s	1430 s	
1465 w	1465 w	1460 w, br
1590 sh	1590 sh	1595 s
1600 vs	1600 vs	
1628 s	1628 s	1620 sh
		1660 m

Table 2. Mass spectra of silated samples separated in chromatograms a, b, c, d of Fig. 4.

Chromatogram	Peak No.	Sample Identification	Base Peak	Other Characteristic Ions
a		t-ferulic acid	338	323, 308, 293, 249, 73
b	1	c-ferulic acid	73	338, 323, 308, 293, 249
	3	t-ferulic acid	73	338, 323, 308, 293, 249
	2,4,5	under analysis[e]	--	----------
	6,7	under analysis[e]	--	----------
c	1	c-ferulic acid	73	338, 323, 308, 293, 249
	3	t-ferulic acid	338	323, 308, 293, 249, 73
	2,4,5	under analysis[e]	--	----------
	6,7	under analysis[e]	--	----------
d	2	palmitic acid	73	328, 313, 145, 132, 117
	4	stearic + oleic acid	73	356, 341, 263, 145, 129
	1,3,5	under analysis[e]	--	----------
	6,7,8	under analysis[e]	--	----------

[e]Perhaps impurity peaks; also seen in solvent run.

Table 3. Brightness data on handsheets.

Handsheet Identification	TAPPI Brightness (%)
Nonyellowed	55.30
Photoyellowed	30.90
Photoyellowed and methanol extracted	31.05
Photoyellowed and laser desorbed	37.30

Table 4. IR peak positions in the region 1800-1500 cm^{-1} for spectra shown in Fig. 7.

A	B	C	D	E
1738	1738	1738		
1680	1687		1684	1681
	1670	1662		
	1631		1625	1625
1593	1599	1599	1594	1599
				1593
1510	1510	1510	1517	1517

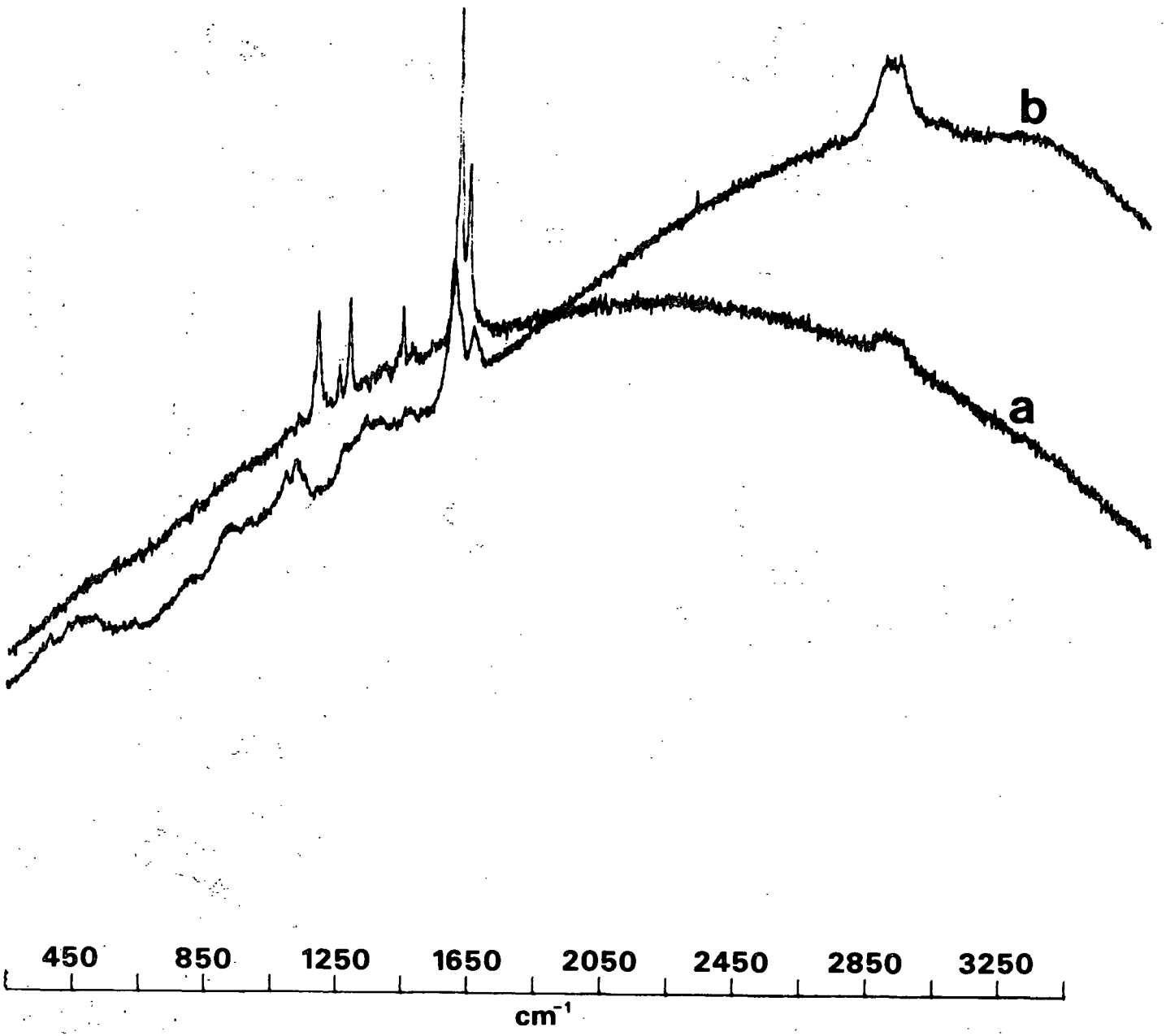


Fig. 1 Raman spectra of yellowed (a) and unyellowed (b) white spruce handsheet samples obtained under molecular oxygen atmosphere.

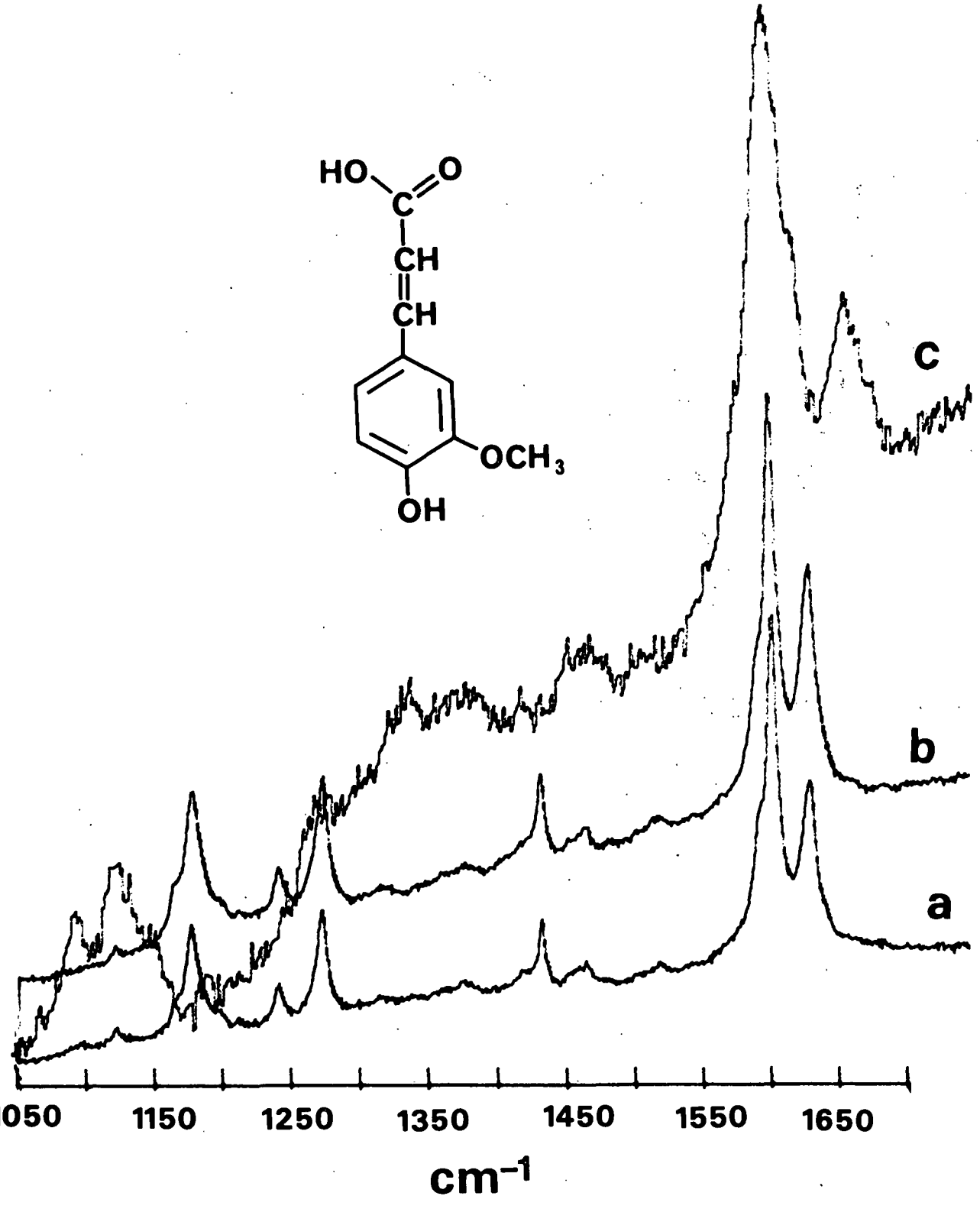


Fig. 2 Raman spectra in the region 1050-1750 cm^{-1} shown on expanded frequency scale; (a) yellowed sheet; (b) ferulic acid; (c) unyellowed sheet. Ferulic acid molecular structure is also shown.

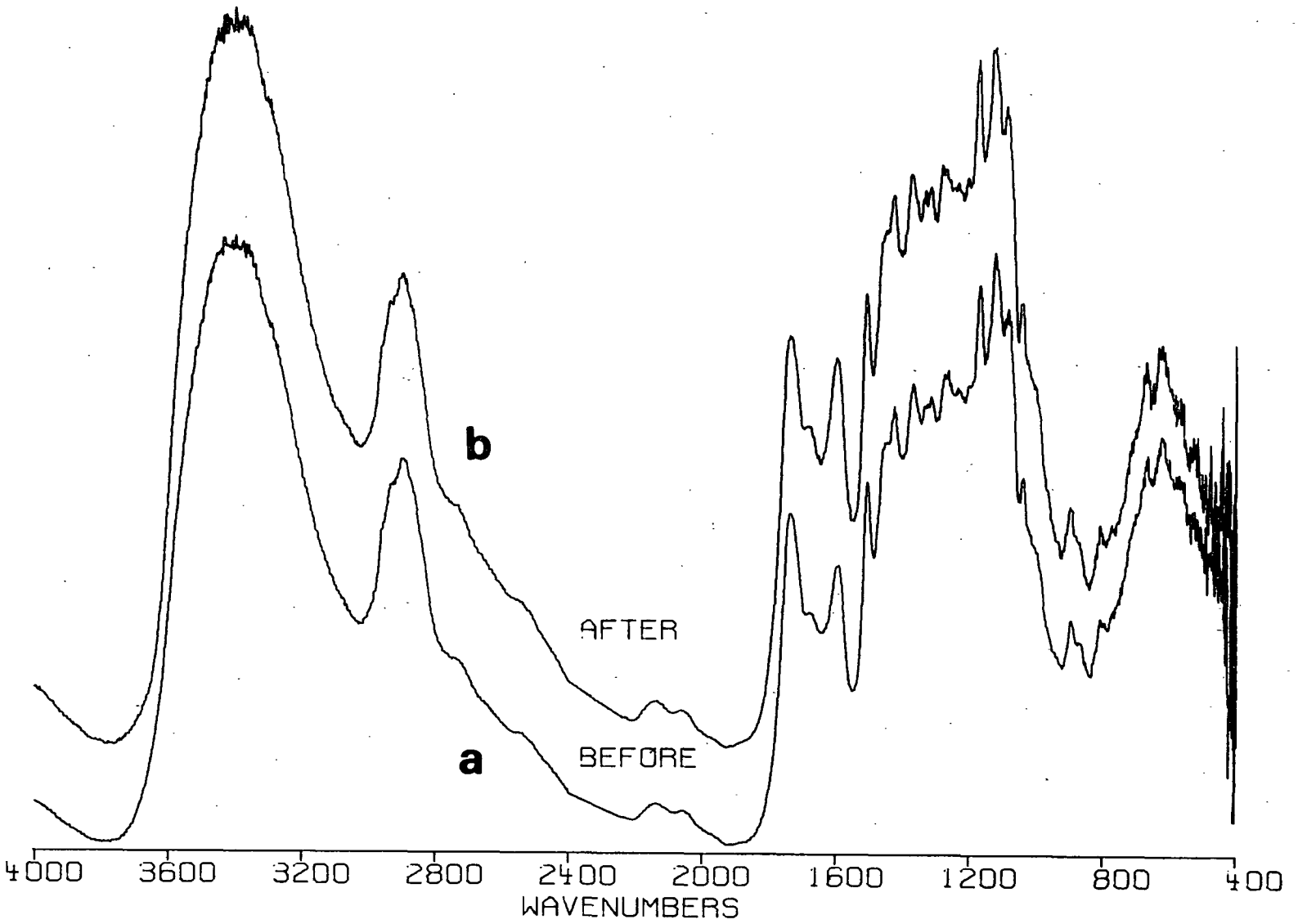


Fig. 3 Typical infrared spectra obtained from yellowed sample (a) before and (b) after Raman experiment.

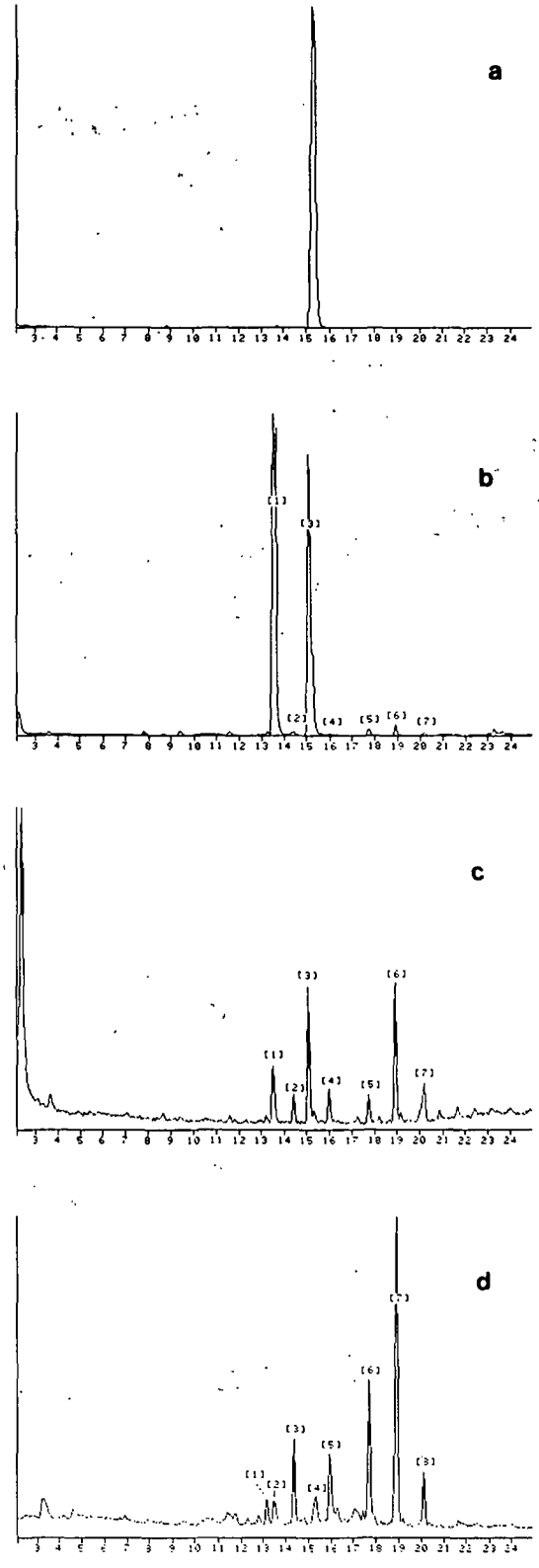
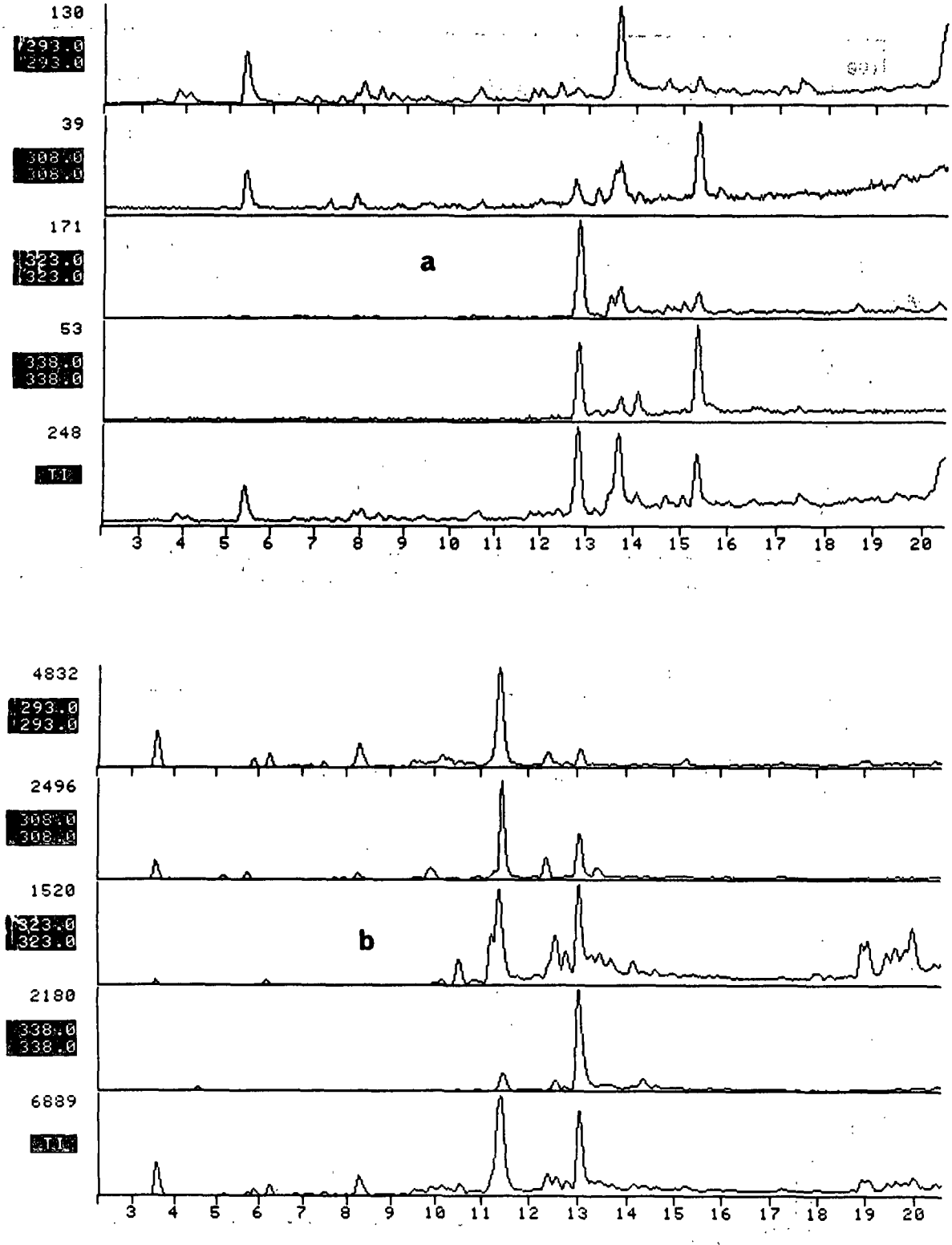


Fig. 4 Chromatograms of silated samples; (a) t-ferulic acid; (b) cis/trans ferulic acid mixture; (c) yellowed handsheet extract; (d) control or nonyellowed handsheet extract.



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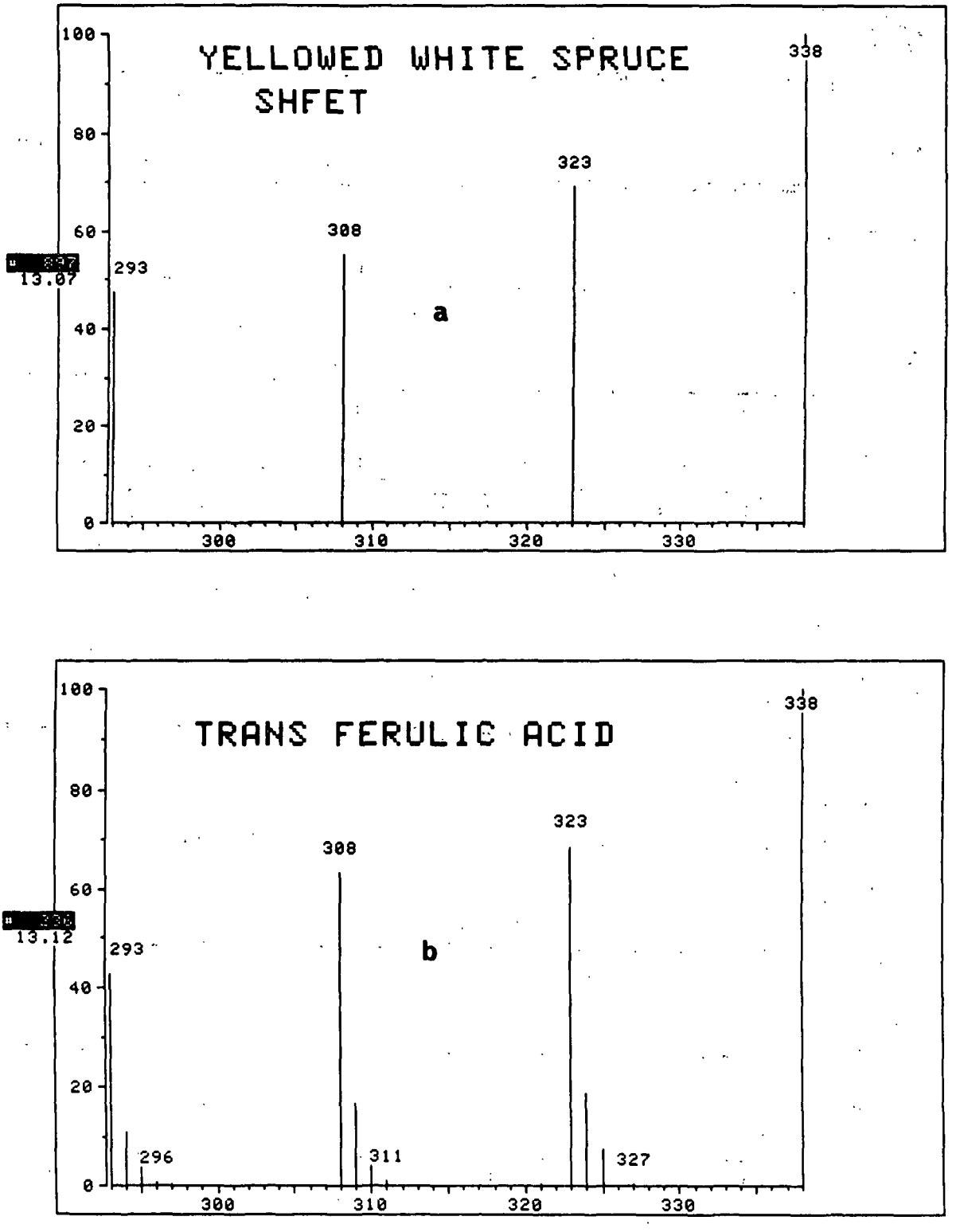

Fig. 6 Relative ion abundances of several ferulic acid ions in (a) yellowed handsheet extract, and (b) trans-ferulic acid.

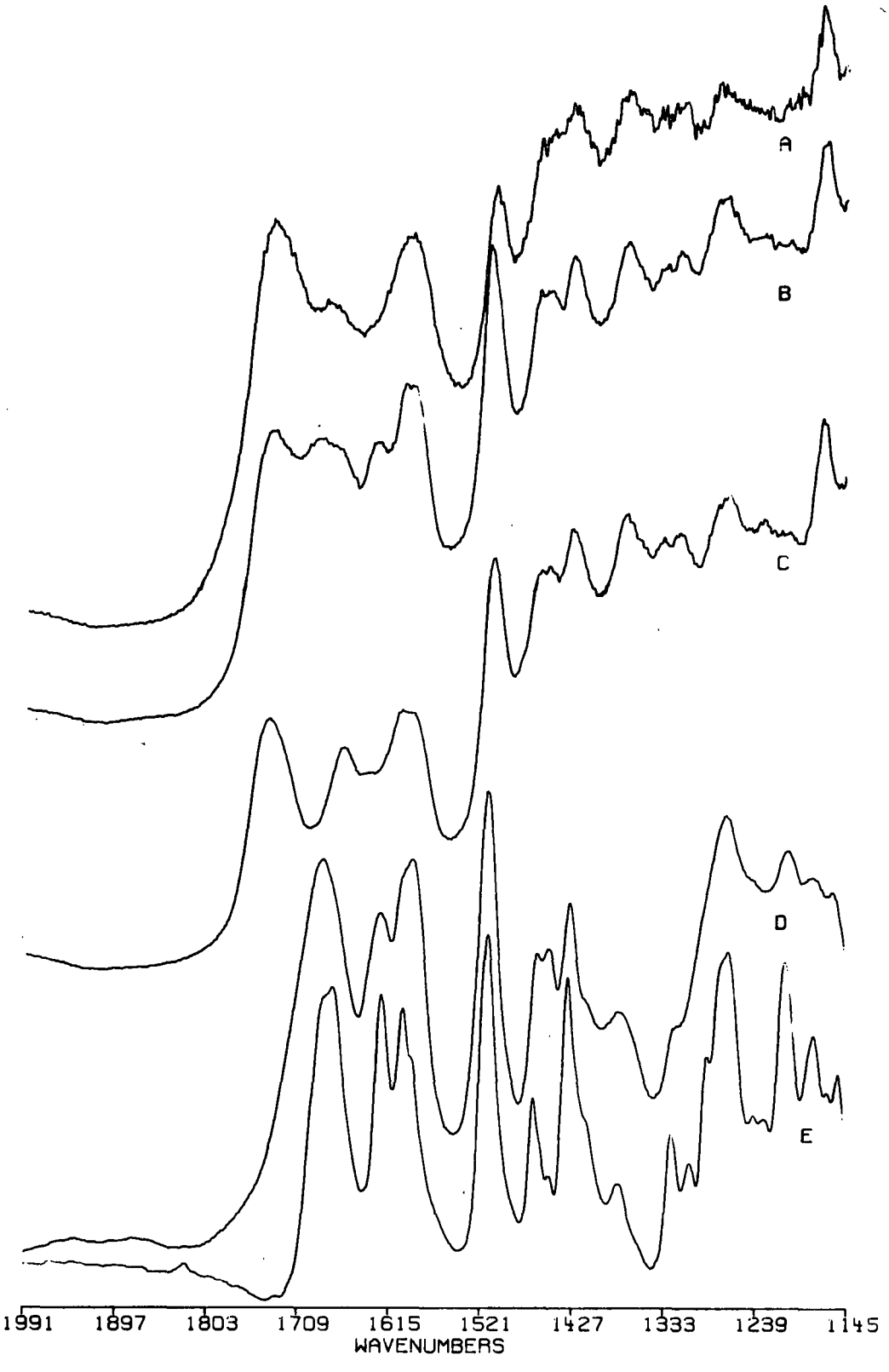

Fig. 7 Infrared spectra of (A) yellowed sheet; (B) unyellowed sheet + (trans-ferulic acid); (C) unyellowed sheet; (D) cis/trans ferulic acid mixture; (E) trans-ferulic acid.